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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US00/01771 <b>(22) International Filing Date:</b> 24 January 2000 (24.01.00) <b>(30) Priority Data:</b> 60/117,095 25 January 1999 (25.01.99) US <b>(71) Applicant (for all designated States except US):</b> UNIVERSITY OF DELAWARE [US/US]; Office of Patents and Research, 210 Hullihen Hall, Newark, DE 19716 (US). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> HUFF, Marilyn, C. [US/US]; 310 Palomino Drive, Newark, DE 19711 (US). FLICK, Derrick, W. [US/US]; 2142D Haven Road, Wilmington, DE 19809 (US). <b>(74) Agent:</b> PEZZNER, Ashley, I.; Connolly Bove Lodge & Hutz LLP, 1220 Market Street, P.O. Box 2207, Wilmington, DE 19899 (US).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> OXIDATIVE DEHYDROGENATION PROCESS AND CATALYST  <b>(57) Abstract</b>  This invention pertains to a catalyst containing a monolith impregnated with a Cr containing compound. In addition, the invention pertains to the production of olefins by the reacting hydrocarbons and an oxygen containing gas in the presence of a catalyst containing a chromium compound, a copper containing compound, a manganese containing compound and a combination thereof supported on a monolith.		

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## OXIDATIVE DEHYDROGENATION PROCESS AND CATALYST

### CROSS REFERENCE TO RELATED APPLICATIONS

5 This application is claims benefit to provisional application 60/117,095 filed January 25, 1999, which is incorporated by reference in its entirety for all useful purposes.

### FIELD OF THE INVENTION

10 This invention pertains to the production of olefins by the oxidative dehydrogenation or cracking of saturated hydrocarbons over a catalyst containing chromium and/or chromium oxide. High yields of olefins can be obtained over structured catalysts with very short contact times and no catalyst deactivation.

### BACKGROUND OF INVENTION

15 Currently, olefins are used as important chemical intermediates for a large number of industrial processes and consumer products. These light olefins such as ethylene, propylene, and butenes are usually produced by the steam pyrolysis process [*Pyrolysis: Theory and Industrial Practice*; Albright, L. F. et al, Eds.; Academic Press: New York, 1983]. The two major limitations of the current steam pyrolysis process are  
20 the high gas temperatures (800-900°C) required and the deposition of coke on the walls of the reactor tube that require the periodic shut-down of the process for decoking. To overcome these limitations, there has been much recent interest in trying to find a catalytic alternative to the current industrial steam cracking process.

25 Many researchers have investigated the catalytic dehydrogenation of light alkanes as a route to obtaining alkenes for polymerization and other organic synthesis. This approach does not cofeed an oxidant. Much of this research has focused on

E., *J. Catal.* **1993**, *142*, 166-171; Hoang, M.; Hughes, A. E. et al, *J. Catal.* **1997**, *171*, 313-319; Hoang, M. et al, *React. Kinet. Catal. Lett.* **1997**, *61*, 21-26; Zaki, M. I. et al, *Appl. Catal.* **1986**, *21*, 359-377]. Thus, the catalytic properties of supported chromium catalysts are strongly affected by the acidity/basicity of the oxide support. However, there is significant disagreement over the exact oxidation state of the active Cr surface species. Recent research has also examined the use of supported chromium oxide catalysts for the catalytic dehydrogenation of hydrocarbons [De Rossi, S. et al, *Appl. Catal. A: General* **1992**, *81*, 113-132; De Rossi, S. et al, *Appl. Catal. A: General* **1993**, *106*, 125-141; De Rossi, S. et al, *J. Catal.* **1994**, *148*, 36-46; Lugo, H. J. and Lunsford, J. H., *J. Catal.* **1985**, *91*, 155-166; Udomsak, S. and Anthony, R. G., *Ind. Eng. Chem Res.* **1996**, *35*, 47-53].

#### **SUMMARY OF THE INVENTION**

This invention describes the production of olefins by catalytic partial oxidation of saturated hydrocarbons on chromium oxide supported on monoliths at very short contact times. This catalyst and process can be significantly less expensive to operate than either a standard packed bed reactor using a selective oxide catalyst at a residence time in excess of 0.1 seconds or the newer short contact time oxidative dehydrogenation process using monolithically supported noble metals. Additionally, this catalyst produces less by-product CO which is advantageous to downstream processes. The monoliths may be composed of any oxide stable at temperature in excess of 900°C including  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Mg-stabilized ZrO<sub>2</sub>, and Y-stabilized ZrO<sub>2</sub> and may have a honeycomb or foam structure although the foam structure is preferred. The support affects the activity of the chromium oxide catalyst as does the presence of various promoters, including Cu, Mn, Mg, Ni, Fe, their oxides, and combinations

thereof. The preferred promoters are copper and copper oxides. The preferred metal atom ratio of promoter to chromium is between 1:100 and 1:2 and more preferably between 1:15 and 1:5.

To summarize these results, supported chromium oxide has been shown to be an effective catalyst for the oxidative dehydrogenation of ethane. As reported in the literature, the activity of the supported chromium oxide catalyst has been shown to depend upon the ceramic support material [Hoang, M. et al, *J. Catal.* 1997, 171, 313-319], the surface area, and the chromium oxide loading (with a lower loading showing a lower activity and shorter lifetime). The high loading chromium oxide catalyst supported on ZrO<sub>2</sub> monolith showed the best overall activity of all the supported chromium oxide catalysts, but could not achieve stable operation at flow rates higher than 5 SLPM. The 9 wt. % Cr<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalyst outperformed the Pt-coated monolith with a higher C<sub>2</sub>H<sub>4</sub> selectivity and C<sub>2</sub>H<sub>6</sub> conversion, and thus higher C<sub>2</sub>H<sub>4</sub> yield. It was also found that the addition of copper to the chromium oxide on ZrO<sub>2</sub> catalyst significantly increased the activity of the catalyst such that stable operation with no signs of deactivation was with GHSV (STP) up to  $1 \times 10^6 \text{ hr}^{-1}$ . The addition of copper to the Cr<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalyst, however, did not significantly affect the product selectivity or reactant conversions.

#### DETAILED DESCRIPTION OF INVENTION

Any short contact time reactor can be used. The reactor used here is essentially identical to that previously described for the production of syngas [Hickman, D. A. and Schmidt, L. D., *J. Catal.* 1992, 136, 300-308 and references therein] and oxidative dehydrogenation of light alkanes [Flick, D. W. and Huff, M. C., *J. Catal.* 1998, 178, 315-327 and references therein; Huff, M. and Schmidt, L. D., *J. Phys. Chem.* 1993, 97,

11815-11822 and references therein]. The reactor consists of a quartz tube with an inner diameter of 20 mm. The catalyst is sealed in the tube with high temperature silica-alumina felt which prevents the bypass of gases around the catalyst. To reduce the radiation heat loss in the axial and radial directions and to better approximate adiabatic operation, inert foam monoliths are placed in front and behind the catalyst as heat shields, and the reaction zone is externally insulated.

A ceramic foam monolith with 20-100 pores per linear inch (ppi) is impregnated with a Cr containing precursor such as an aqueous solution of  $\text{Cr}(\text{NO}_3)_3$ , and then calcined in air at  $600^\circ\text{C}$  for at least four hours. After calcination, the chromium oxide coated monoliths were bright green in color. The chromium oxide can be supported on monoliths made from high temperature ( $>900^\circ\text{C}$ ) stable oxides including  $\alpha\text{-Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , Mg-stabilized  $\text{ZrO}_2$ , and Y-stabilized  $\text{ZrO}_2$ . Pt and mixtures of promoters (Cu, Mn, Mg, Ni, Fe, and combinations thereof) were deposited on the monoliths similarly using  $\text{H}_2\text{PtCl}_6$  or transition metal nitrate salts, respectively, in an aqueous solution. The monoliths used measured 10 mm thick and between 18-20 mm in diameter.

The gas flow for the reactor is controlled by electronic mass flow controllers. The total feed flow rate to the reactor ranged from 0.1 to 12 SLPM which corresponds to approximate contact times of 2-200 milliseconds ( $\text{GHSV} = 1 \times 10^5 - 2.2 \times 10^6 \text{ hr}^{-1}$  at STP) for the monolith catalyst. The reactor operates near atmospheric pressure. The reaction occurs autothermally around  $900^\circ\text{C}$ .

While the reaction operates autothermally at steady state, an external heat source is necessary to ignite the reaction. The gas mixture with  $\text{C}_2\text{H}_6:\text{O}_2:\text{N}_2 = 25:15:60$  ignites at approximately  $350^\circ\text{C}$  over the chromium oxide catalyst at a flow rate of 3 SLPM which is higher than the  $220^\circ\text{C}$  preheat needed to ignite that reaction over a Pt coated monolith catalyst. After ignition, the external heat source is removed or



reduced to the desired level of heat addition, the composition is adjusted to the desired value and steady state is established. After each change in feed conditions, the reactor is allowed to achieve steady state (<10 min.) before analysis of the reaction products by the GC.

5 The feed gas consists of  $C_2H_6$  and  $O_2$  with  $N_2$  as the diluent. The level of dilution ranged from <1 to about 80%. The  $N_2$  was used as an internal GC calibration standard. Additional trials have been completed using alternative diluents:  $N_2$ , He, Ar,  $CO_2$ ,  $H_2O$  and mixtures thereof. Some experiments were conducted with the feed composition within the flammability limits. In these instances, it is important to realize  
10 that this is a flow system with linear velocities in excess of the flame speed such that homogeneous ignition is impossible [Bolk, J. W. et al, *Chem. Eng. Sci.* 1996, 51].

The reaction temperature was measured by a type K (chromel/alumel) thermocouple inserted from the rear of the reactor and placed at the center of the reactor tube between the catalyst and the rear radiation heat shield. The temperature  
5 measured at the back of the catalyst, the reaction temperature, is a good measure of both the product gas phase temperature and the surface temperature of the rear face of the catalyst, since the gas phase and surface temperatures are approaching equilibrium at the catalyst exit.

In some experiments, the feed gas to the reactor contained  $C_2H_6$ ,  $O_2$ , and  $H_2$   
20 with a small amount of  $N_2$  for use as an internal calibration standard. The level of  $H_2$  in the feed ranged from 0 to 50% which corresponds to  $H_2/O_2$  ratios ranging from 0 to 3.0. The amount of  $N_2$  in the feed was always less than 1%. The process could recycle the  $H_2$  and not require a net import of  $H_2$  to the system.

The catalyst can contain substantially no Pt. Substantially no Pt means less than  
25 0.1% Pt by weight, preferably less than 0.01 % Pt by weight.

Table 7: Carbon atom and hydrogen atom selectivity, conversion, and temperature for ethane oxidation over a 45 ppi, 4 wt. %  $\text{Cr}_2\text{O}_3/\text{ZrO}_2$  monolith as a function of flow rate at a  $\text{C}_2\text{H}_6/\text{O}_2$  ratio of 1.5 with 20%  $\text{N}_2$  dilution in an autothermal reactor at a pressure of 1.2 atm.

Flowrate (SLPM)	1	2	3
Carbon atom selectivity (%)			
$\text{C}_2\text{H}_4$	56.6	51.7	48.2
CO	22.8	23.1	24.7
$\text{CO}_2$	9.8	7.9	7.7
$\text{CH}_4$	7.5	9.8	9.8
$\text{C}_2\text{H}_2$	0.01	0.9	6.1
Other	3.3	6.6	3.5
Hydrogen atom selectivity (%)			
$\text{H}_2$	34.7	36.6	42.7
$\text{H}_2\text{O}$	24.7	21.8	16.0
Conversion (%)			
$\text{C}_2\text{H}_6$	89.5	92.3	93.3
$\text{O}_2$	99.5	99.4	99.7
Temperature ( $^{\circ}\text{C}$ )			
Front	1025	1053	367
Rear	840	895	954

Table 8: Carbon atom and hydrogen atom selectivity, conversion, and temperature for ethane oxidation over a 45 ppi, 6.7% Cu - 6.7%  $\text{Cr}_2\text{O}_3/\text{ZrO}_2$  monolith as a function of flow rate at a  $\text{C}_2\text{H}_6/\text{O}_2$  ratio of 2.4 with 20%  $\text{N}_2$  dilution in an autothermal reactor at a pressure of 1.2 atm.

Flowrate (SLPM)	2	3	4
Carbon atom selectivity (%)			
$\text{C}_2\text{H}_4$	71.4	69.9	67.1
CO	7.3	7.3	7.2
$\text{CO}_2$	14.1	11.8	11.3
$\text{CH}_4$	3.6	3.9	3.7
$\text{C}_2\text{H}_2$	0.5	0.7	0.4
Other	3.0	6.5	10.2
Hydrogen atom selectivity (%)			
$\text{H}_2$	16.3	17.3	15.9
$\text{H}_2\text{O}$	28.4	24.0	23.3
Conversion (%)			
$\text{C}_2\text{H}_6$	58.0	64.4	65.0
$\text{O}_2$	99.8	99.7	99.6
Temperature ( $^{\circ}\text{C}$ )			
Front	245	146	108
Rear	738	760	756

could not be sustained for even a few minutes. Thus, for the  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  catalyst, the reaction can only be sustained inside the flammability range for the  $\text{C}_2\text{H}_6$ ,  $\text{O}_2$ , and  $\text{N}_2$  system, and the lifetime decreases the closer the mixture is to the upper flammability boundary. However, in stark contrast to the  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  catalyst, the 9 wt. %  $\text{Cr}_2\text{O}_3/\text{ZrO}_2$  monolith sustained steady reaction up to a  $\text{C}_2\text{H}_6/\text{O}_2$  ratio of 1.8 with 50%  $\text{N}_2$  dilution for over 2 hours and at a  $\text{C}_2\text{H}_6/\text{O}_2$  ratio of 1.5 with 50%  $\text{N}_2$  dilution at 2 SLPM, the Cu modified  $\text{Cr}_2\text{O}_3/\text{ZrO}_2$  monolith catalyst did not show any deactivation for over 7 hours of continuous operation, while all of the previous chromium oxide containing catalyst rapidly extinguished at a  $\text{C}_2\text{H}_6/\text{O}_2$  ratio of 1.5 with 50%  $\text{N}_2$  dilution.

The effects of preheat are shown in Tables 9-10 for the 9 wt. %  $\text{Cr}_2\text{O}_3/\alpha\text{-Al}_2\text{O}_3$  monolith catalyst at a  $\text{C}_2\text{H}_6/\text{O}_2$  ratio of 1.5 with 20%  $\text{N}_2$  dilution at a flowrate of 2 SLPM. Results are shown as a function of time for nearly adiabatic operation (Table 9) and for

autothermal operation (Table 10) where the reactants have been heated to 250°C before reaching the reaction zone. Preheat results in a catalyst lifetime of ~7 hours before the reaction extinguished. The addition of preheat, however, leads to a slightly lower selectivity to  $C_2H_4$  and a higher selectivity to CO. Preheating the feed also  
5 increased the selectivity to  $CH_4$  and  $C_2H_2$  and decreased the selectivity to  $CO_2$ . As expected, the  $C_2H_6$  conversion increases with preheat.

The most interesting impact of preheat is shown in the temperature of the catalysts. The front and back temperature of the catalyst without preheat and the front temperature of the catalyst with preheat fall dramatically after approximately 1.5 hours  
10 of operation. However, the addition of preheat seems to provide enough energy to keep the reaction ignited with relatively stable front and back temperatures over the catalyst for several hours after the catalyst without preheat extinguished. The 250°C preheat of the feed, however, did not provide enough energy to keep the reaction from eventually extinguishing. There were also slight selectivity changes to  $C_2H_4$ ,  $CH_4$ , and CO that  
15 correspond with the rapid drop in the temperature at the front of the catalyst.

Table 9: Carbon atom and hydrogen atom selectivity, conversion, and temperature for ethane oxidation over a 45 ppi, 9 wt. %  $\text{Cr}_2\text{O}_3/\alpha\text{-Al}_2\text{O}_3$  monolith as a function of time at a  $\text{C}_2\text{H}_6/\text{O}_2$  ratio of 1.5 with 20%  $\text{N}_2$  dilution in an autothermal reactor at a pressure of 1.2 atm. Data is shown for reactants entering the reactor at room temperature.

Time on stream (hr)	0.0	0.5	1.0	1.5	
Carbon atom selectivity (%)					
$\text{C}_2\text{H}_4$	41.8	46.2	46.6	42.8	Extinguished after ~1.7 hrs.
CO	27.8	25.5	26.6	32.4	
$\text{CO}_2$	6.8	8.6	8.2	7.2	
$\text{CH}_4$	11.3	10.1	10.0	11.1	
$\text{C}_2\text{H}_2$	8.3	5.8	5.0	3.6	
Other	4.0	3.8	3.6	2.9	
Hydrogen atom selectivity (%)					
$\text{H}_2$	42.1	42.0	43.1	43.3	
$\text{H}_2\text{O}$	17.2	17.1	16.4	17.2	
Conversion (%)					
$\text{C}_2\text{H}_6$	97.6	95.8	95.1	88.6	
$\text{O}_2$	100	99.8	99.8	99.2	
Temperature ( $^{\circ}\text{C}$ )					
Front	390	187	164	56	
Rear	1015	1025	998	870	

Table 10: Carbon atom and hydrogen atom selectivity, conversion, and temperature for ethane oxidation over a 45 ppi, 9 wt. %  $\text{Cr}_2\text{O}_3/\alpha\text{-Al}_2\text{O}_3$  monolith as a function of time at a  $\text{C}_2\text{H}_6/\text{O}_2$  ratio of 1.5 with 20%  $\text{N}_2$  dilution in an autothermal reactor at a pressure of 1.2 atm. Data is shown for reactants entering the reactor at  $250^{\circ}\text{C}$  temperature. The reaction extinguished between hours 7 and 8.

Time on stream (hr)	0.0	0.5	1.0	1.5	2.0	4.0	6.0	7.0
Carbon atom selectivity (%)								
$\text{C}_2\text{H}_4$	36.3	36.6	36.5	39.1	40.5	40.4	41.1	37.0
CO	33.2	34.0	34.6	30.0	29.9	30.7	29.5	37.2
$\text{CO}_2$	5.0	4.7	4.3	3.5	3.3	3.3	2.9	3.5
$\text{CH}_4$	13.2	13.0	13.0	14.0	14.4	14.3	14.4	12.8
$\text{C}_2\text{H}_2$	9.1	8.4	7.8	7.9	7.7	7.3	6.6	5.8
Other	3.2	3.3	3.8	5.5	4.2	4.0	5.5	3.7
Hydrogen atom selectivity (%)								
$\text{H}_2$	46.8	47.2	47.6	42.9	42.8	42.9	40.7	50.8
$\text{H}_2\text{O}$	14.6	14.4	14.1	14.1	14.4	14.5	15.1	10.8
Conversion (%)								
$\text{C}_2\text{H}_6$	98.5	98.3	98.2	98.0	97.9	97.9	97.5	97.8
$\text{O}_2$	99.9	99.9	99.9	99.9	99.9	99.9	99.9	99.9
Temperature ( $^{\circ}\text{C}$ )								
Front	1180	1132	1112	670	640	595	580	565
Rear	1000	962	895	870	840	825	818	760

**Example 6:** The oxidative dehydrogenation of ethane was investigated with different diluents including N<sub>2</sub>, Ar, CO<sub>2</sub> and H<sub>2</sub>O. The carbon and hydrogen atom selectivities, conversions and temperatures for the oxidative dehydrogenation over a 1.0 wt. % Cu – 9.0 wt. % Cr<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalyst at C<sub>2</sub>H<sub>6</sub>/O<sub>2</sub> ratios of 1.8 and 2.4 at a total flow rate of 2 SLPM with 20% dilution are shown in Tables 11 and 12. The product selectivities are not significantly affected by changes in the type of diluent. The ethane conversion,

Table 11. Carbon and hydrogen atom selectivity, conversion, and temperature for ethane oxidative dehydrogenation over a 1.0 wt. % Cu – 9.0 wt. % Cr<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalyst at a C<sub>2</sub>H<sub>6</sub>/O<sub>2</sub> ratio of 1.8 with 20% total dilution at a total flow rate of 2 SLPM in an autothermal reactor at a pressure of 1.2 atm.

Diluent (% of total feed)				
N <sub>2</sub>	20	2.5	2.5	10
Ar	0	17.5	0	0
CO <sub>2</sub>	0	0	17.5	0
H <sub>2</sub> O	0	0	0	10
Carbon atom selectivity (%)				
C <sub>2</sub> H <sub>4</sub>	62	61	65	63
CO	16	16	17	16
CO <sub>2</sub>	8	9	7	8
CH <sub>4</sub>	7	8	7	7
C <sub>2</sub> H <sub>2</sub>	3	4	1	3
Other	4	2	3	3
Hydrogen atom selectivity (%)				
H <sub>2</sub>	22	22	22	23
H <sub>2</sub> O	21	21	24	22
Conversion (%)				
C <sub>2</sub> H <sub>6</sub>	89	90	86	88
O <sub>2</sub>	100	100	100	100
Temperature (°C)				
Front	848	942	594	674
Rear	900	862	850	882

Table 12. Carbon and hydrogen atom selectivity, conversion, and temperature for ethane oxidative dehydrogenation over a 1.0 wt. % Cu – 9.0 wt. % Cr<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalyst at a C<sub>2</sub>H<sub>6</sub>/O<sub>2</sub> ratio of 2.4 with 20% total dilution at a total flow rate of 2 SLPM in an autothermal reactor at a pressure of 1.2 atm.

Diluent (% of total feed)				
N <sub>2</sub>	20	2.5	2.5	10
Ar	0	17.5	0	0
CO <sub>2</sub>	0	0	17.5	0
H <sub>2</sub> O	0	0	0	10
Carbon atom selectivity (%)				
C <sub>2</sub> H <sub>4</sub>	72	72	72	73
CO	9	10	9	8
CO <sub>2</sub>	11	11	11	12
CH <sub>4</sub>	4	4	3	4
C <sub>2</sub> H <sub>2</sub>	1	1	0	1
Other	3	2	3	3
Hydrogen atom selectivity (%)				
H <sub>2</sub>	18	20	17	16
H <sub>2</sub> O	25	24	27	27
Conversion (%)				
C <sub>2</sub> H <sub>6</sub>	64	62	57	59
O <sub>2</sub>	100	100	100	100
Temperature (°C)				
Front	257	657	412	421
Rear	834	796	794	839

however, does change slightly with different diluents. Along with the decrease in ethane conversion, the reaction temperature at the back of the catalyst is also lower with the CO<sub>2</sub> and H<sub>2</sub>O diluent. Therefore, use of diluents with different heat capacities has the effect of lowering the ethane conversion and temperature at the back of the catalyst with increases in the heat capacity of the diluent used. The use of CO<sub>2</sub> and H<sub>2</sub>O which are reaction products in the oxidative dehydrogenation of ethane as the diluent does not significantly affect the product selectivities under these reaction conditions.

**Example 7:** Table 13 shows typical reactor performance for the oxidative dehydrogenation of propane over a variety of monolithic catalysts at nitrogen dilutions levels of 20% and 50% at total flow rate of 2 SLPM. The less expensive chromium oxide catalyst shows similar selectivity and conversion trends as the Pt catalyst with significantly less production of CO.

Table 13: Carbon atom and hydrogen atom selectivity, conversion, and temperature for propane oxidation over various catalysts at several C<sub>3</sub>H<sub>8</sub>/O<sub>2</sub> ratios with 20% and 50% N<sub>2</sub> dilution and a total flow rate of 2 SLPM in an autothermal reactor at a pressure of 1.2 atm.

Catalyst	6 wt. % Cr <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>								6 wt. % Pt/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>							
N <sub>2</sub> dilution (%)	20				50				20				50			
C <sub>3</sub> H <sub>8</sub> /O <sub>2</sub>	1.2	1.5	1.8	2.0	1.2	1.5	1.8		1.2	1.5	1.8	2.0	1.2	1.5	1.8	2.0
Carbon atom selectivity (%)																
C <sub>3</sub> H <sub>6</sub>	1.2	10.3	20.7	26.0	1.1	11.0	22.7		2.8	16.0	23.5	27.7	1.1	15.1	22.6	26.1
C <sub>2</sub> H <sub>4</sub>	37.8	45.5	40.7	37.7	34.6	43.1	34.3		37.7	38.7	33.4	32.1	31.3	37.3	29.2	23.8
CO	21.0	9.1	6.3	5.3	23.3	11.0	9.2		26.6	17.0	16.5	13.9	33.6	17.8	18.5	20.7
CO <sub>2</sub>	7.5	8.2	9.0	9.9	9.1	10.9	15.5		3.8	4.1	6.1	6.8	5.8	7.9	12.2	15.0
CH <sub>4</sub>	23.3	19.8	16.8	15.6	21.7	17.0	13.0		22.6	18.4	15.7	15.1	20.7	16.7	13.4	11.2
C <sub>2</sub> H <sub>6</sub>	1.1	2.6	2.5	2.3	0.7	2.4	2.1		1.6	2.4	2.1	2.0	0.9	2.2	1.9	1.5
C <sub>2</sub> H <sub>2</sub>	5.9	1.5	0.8	0.5	7.4	2.0	0.5		3.1	0.8	0.1	0.1	4.5	0.5	0.2	0.1
Other	2.1	2.9	3.1	2.8	2.3	2.6	2.7		1.8	2.6	2.6	2.2	2.1	2.6	2.1	1.6
Hydrogen atom selectivity (%)																
H <sub>2</sub>	20.1	9.5	7.4	6.5	19.4	10.0	7.9		16.4	8.2	6.9	5.6	19.9	8.6	8.2	6.8
H <sub>2</sub> O	13.4	15.9	16.9	17.9	18.9	19.3	26.1		17.5	19.5	24.7	24.6	21.5	23.0	29.5	36.3
Conversion (%)																
C <sub>3</sub> H <sub>8</sub>	99.9	92.3	74.3	60.8	100	91.5	64.0		99.3	83.3	63.8	52.5	99.9	83.1	57.1	39.3
O <sub>2</sub>	100	99.5	99.1	99.1	100	99.7	98.9		99.3	98.2	97.7	97.8	99.4	98.4	98.0	97.7
Temperature (°C)																
Front	1066	678	584	529	1027	623	500		980	622	545	505	1018	941	921	849
Rear	965	875	829	808	934	852	800		969	909	876	866	937	831	825	815

surveying a wide variety of metal oxides for high selectivity and conversion [Carra, S. and Fomi, L., *Catal. Rev.* **1971**, *5*, 159-198; Cimino, A. et al, *J. Mol. Catal.* **1989**, *55*, 23-33; US Patent #4535067; US Patent #4804799; US Patent #3965044; US Patent #5354935; US Patent #5254788; US Patent #5378350; US Patent #3719721; US Patent #4032589]. However, these catalysts generally deactivate with time on stream due to coke build-up on the catalyst surface [Royo, C. et al, *Ind. Eng. Chem. Res.* **1994**, *33*, 2563-2570].

Catalytic oxidative dehydrogenation of hydrocarbons is an alternative to thermal pyrolysis and catalytic dehydrogenation. The oxidative dehydrogenation of C<sub>2</sub>-C<sub>6</sub> hydrocarbons has been examined over noble metal catalysts supported on ceramic foam monoliths [ Flick, D. W. and Huff, M. C., *Appl. Catal. A* **1999** *187*, 13-24; Flick, D. W. and Huff, M. C., *Abstracts of Papers of ACS 217:O18-CATL*, Part 2 March 21, 1999; Flick, D. W. and Huff, M. C., *Catal Lett* **1997**, *47*, 91-97; Flick, D. W. and Huff, M. C., *J. Catal.* **1998**, *178*, 315-327; Dietz III, A. G. et al, *J. Catal.* **1998**, *176*, 459-473; Huff, M. C. et al, *Catal. Today* **1994**, *21*, 113-128; US Patent # 5905180 which are all incorporated by reference in its entirety for all useful purposes]. In general, noble metal catalysts are more expensive than oxide catalysts. The oxidative dehydrogenation of ethane over Pt-coated monolith catalysts at short contact times has been investigated concerning the maximization of C<sub>2</sub>H<sub>4</sub> production [US Patent #5382741; US Patent #5625111; Huff, M. and Schmidt, L. D., *J. Phys. Chem.* **1993**, *97*, 11815-11822; US Patent #4844837; US Patent #4940826; US Patent #5105052; US Patent #5593935; Witt, P. M. and Schmidt, L. D., *J. Catal.* **1996**, *163*, 465-475; US Patent # 5905180]. These monolith reactors operate at very short contact times on the order of milliseconds. The yield of C<sub>2</sub>H<sub>4</sub> with these reactors has been shown to be about 50% (C<sub>2</sub>H<sub>4</sub> selectivity ~65% at around 80% conversion).

**Example 8:** Table 14 shows typical reactor performance for the oxidative dehydrogenation of butane over a variety of monolithic catalysts at nitrogen dilution levels of 20% at total flow rate of 2 SLPM. Again, the less expensive chromium oxide catalyst shows similar selectivity and conversion trends with changes in the fuel to oxygen ratio as the Pt catalyst. In general, the chromium oxide catalysts have a higher conversion of the hydrocarbon and selectivity to  $C_2H_4$  than the Pt catalyst. The chromium oxide catalysts produce less CO especially at the higher fuel to oxygen ratios.

Table 14: Carbon atom and hydrogen atom selectivity, conversion, and temperature for butane oxidation over various catalysts at several  $C_4H_{10}/O_2$  ratios with 20% dilution and a total flow rate of 2 SLPM in an autothermal reactor at a pressure of 1.2 atm.

Of 1.2 atm.								
Catalysts	3 wt. % Pt/Al <sub>2</sub> O <sub>3</sub>	1 wt% Cu - 9 wt% Cr <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>	2 wt% MnOx - 1 wt% Cu - 10 wt% Cr <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>	5 wt% MgO -1 wt% Cu - 10 wt% Cr <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>	3 wt. % Pt/Al <sub>2</sub> O <sub>3</sub>	1 wt% Cu - 9 wt% Cr <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>	2 wt% MnOx - 1 wt% Cu - 10 wt% Cr <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>	5 wt% MgO -1 wt% Cu - 10 wt% Cr <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>
C <sub>4</sub> H <sub>10</sub> /O <sub>2</sub> ratio	1.5				2.0			
Carbon atom selectivity (%)								
C <sub>4</sub> H <sub>10</sub>	1	0	1	1	6	5	6	4
C <sub>3</sub> H <sub>6</sub>	16	7	15	12	30	26	26	28
C <sub>2</sub> H <sub>4</sub>	39	46	39	42	20	25	24	26
CO	17	13	18	16	8	6	6	5
CO <sub>2</sub>	4	8	6	7	19	17	20	20
CH <sub>4</sub>	15	16	15	15	11	10	10	11
C <sub>2</sub> H <sub>6</sub>	3	2	3	3	3	3	3	3
C <sub>2</sub> H <sub>2</sub>	1	1	1	2	0	0	0	0
Other	3	7	3	3	3	8	4	4
Hydrogen atom selectivity (%)								
H <sub>2</sub>	6	11	10	11	2	4	4	4
H <sub>2</sub> O	14	10	12	11	23	17	22	18
Conversion (%)								
C <sub>4</sub> H <sub>10</sub>	93	99	93	95	28	37	30	33
O <sub>2</sub>	98	100	100	99	98	100	100	100
Temperature (°C)								
Front	512	542	999	966	140	68	390	367
Rear	861	870	751	820	713	724	657	702



**Example 9:** Table 15 shows typical reactor performance for the oxidative dehydrogenation of isobutane over a variety of monolithic catalysts at nitrogen dilution levels of 20% at total flow rate of 2 SLPM. Again, the less expensive chromium oxide catalyst shows similar selectivity and conversion trends with changes in the fuel to oxygen ratio as the Pt catalyst. In general, the chromium oxide catalysts have a higher conversion of the hydrocarbon and selectivity to  $C_2H_4$  than the Pt catalyst. The chromium oxide catalysts produce less CO especially at the higher fuel to oxygen ratios.

Table 15: Carbon atom and hydrogen atom selectivity, conversion, and temperature for isobutane oxidation over various catalysts at several  $i-C_4H_{10}/O_2$  ratios with 20% dilution and a total flow rate of 2 SLPM in an autothermal reactor at a pressure of 1.2 atm.

Catalysts	3 wt. % Pt/Al <sub>2</sub> O <sub>3</sub>	1wt% Cu - 9 wt% Cr <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>	2 wt% Ni - 1wt% Cu - 10 wt% Cr <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>	3 wt. % Pt/Al <sub>2</sub> O <sub>3</sub>	1wt% Cu - 9 wt% Cr <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>	2 wt% Ni - 1wt% Cu - 10 wt% Cr <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>
i-C <sub>4</sub> H <sub>10</sub> /O <sub>2</sub> ratio	1.5			2.0		
Carbon atom selectivity (%)						
i-C <sub>4</sub> H <sub>10</sub>	19	11	11	27	22	23
C <sub>4</sub> H <sub>10</sub>	2	2	3	1	4	2
C <sub>3</sub> H <sub>6</sub>	27	27	32	27	31	33
C <sub>2</sub> H <sub>4</sub>	6	14	13	2	5	6
CO	11	12	12	19	8	7
CO <sub>2</sub>	7	8	8	11	12	12
CH <sub>4</sub>	15	19	18	11	14	14
Other	14	7	3	2	4	4
Hydrogen atom selectivity (%)						
H <sub>2</sub>	6	7	6	3	4	4
H <sub>2</sub> O	9	7	7	5	6	6
Conversion (%)						
i-C <sub>4</sub> H <sub>10</sub>	71	87	89	44	57	58
O <sub>2</sub>	98	99	99	98	99	99
Temperature (°C)						
Front	900	1033	1023	840	634	984
Rear	830	817	790	788	761	733

In addition to Pt-coated foam monoliths, Yokoyama, et. al. [Yokoyama, C. et al, *Catal Lett* 1996, 38, 181-188; US Patent # 5905180] examined the addition of various metal promoters to Pt-coated foam monoliths for the autothermal oxidative dehydrogenation of ethane at millisecond contact times. Their study found that the addition of Sn and Cu to Pt-monoliths enhanced the C<sub>2</sub>H<sub>4</sub> selectivity and C<sub>2</sub>H<sub>6</sub> conversion with no deactivation or volatilization of the catalyst. For the Pt-Sn catalyst, the ethane conversion increased by up to 6% and the ethylene selectivity increased by up to 5%. For the Pt-Cu catalyst, the conversion and ethylene selectivity were higher than Pt alone, but showed less improvement than the Pt-Sn catalyst.

Researchers have also examined oxidative dehydrogenation over oxide catalysts [US Patent #4658074; US Patent #5430209; US Patent #5439859; US Patent #3862255; US Patent #5759946; US Patent #4026920]. These precesses produce olefins with yields less than 45%.

The activity and selectivity of chromium oxide-supported catalysts in alkane dehydrogenation has been known for many decades [Frey, F. E. and Huppke, W. F., *Ind. Eng. Chem.* 1933, 25, 54; Marcilly, C. and Delmon, B., *J. Catal.* 1972, 24, 336-347]. Due to their importance in hydrogenation, dehydrogenation, and polymerization reactions, chromium-containing heterogeneous catalysts have been studied by a variety of techniques by a large number of researchers in the past several decades. For the supported chromium Phillips polymerization catalyst, much of the research has focused on the structure and oxidation state of the reactive chromium surface species [Zecchina, A. et al, *J. Phys. Chem.* 1975, 79, 966-972; Weckhuysen, B. M. et al, *Chem. Rev.* 1996, 96, 3327-3349]. It is now generally accepted that the catalytic properties of the supported chromium oxide are due to the surface chromium species formed as a result of chromium-support interactions [Kim, D. S. and Wachs, I.

**Example 10:** The copper modified chromium oxide catalyst supported on a zirconia monolith shows excellent stability for the oxidative dehydrogenation of ethane even at high  $C_2H_6/O_2$  ratios and high flow rates where other catalysts tend to deactivate. Typical reactor performance is shown in Table 16.

Table 16: Carbon atom and hydrogen atom selectivity, conversion, and temperature for ethane oxidation over a 45 ppi. 6.7% Cu - 6.7%  $Cr_2O_3/ZrO_2$  monolith as a function of flow rate at several  $C_2H_6/O_2$  ratios with 50%  $N_2$  dilution in an autothermal reactor at a pressure of 1.2 atm.

$C_2H_6/O_2$	1.5					1.8					2.4			
Flowrate (SLPM)	2	3	4	5	6	2	3	4	5	6	2	3	4	5
Carbon atom selectivity (%)														
$C_2H_4$	62.7	59.1	57.8	55.8	55.7	71.0	68.0	67.7	67.8	65.9	66.0	69.2	70.2	70.4
CO	13.4	13.8	14.5	15.0	15.2	7.0	8.8	8.7	8.9	11.7	5.0	5.3	5.5	5.4
$CO_2$	11.1	10.7	10.9	10.8	11.3	14.1	13.3	13.5	13.4	12.9	25.3	20.8	19.0	18.9
$CH_4$	6.6	7.3	8.0	8.4	8.3	4.2	4.8	5.0	5.0	5.5	1.9	2.4	2.7	2.7
$C_2H_2$	3.1	5.6	6.2	6.6	6.0	1.5	2.0	2.0	1.8	0.8	0.2	0.4	0.4	0.4
Other	3.2	3.5	2.7	3.4	3.4	2.3	3.1	3.2	3.1	3.2	1.7	2.0	2.2	2.3
Hydrogen atom selectivity (%)														
$H_2$	16.6	19.6	21.3	22.0	23.3	15.3	17.5	18.5	19.1	18.9	13.1	15.8	16.9	17.3
$H_2O$	27.8	25.2	24.0	22.9	21.2	28.6	26.3	25.5	24.6	25.3	39.8	32.4	29.3	28.8
Conversion (%)														
$C_2H_6$	89.2	92.3	93.4	94.4	94.5	70.5	76.8	77.5	77.8	75.5	37.3	46.2	50.1	50.5
$O_2$	99.9	99.9	99.8	99.8	99.7	99.9	99.8	99.7	99.6	98.8	100	99.9	99.9	99.8
Temperature ( $^{\circ}C$ )														
Front	408	123	171	131	97	441	99	104	96	75	243	160	104	77
Rear	838	878	901	912	906	762	830	841	848	830	777	813	835	856

**Example 11:** The oxidative dehydrogenation of ethane was investigated where the feed gas to the reactor contained  $C_2H_6$ ,  $O_2$ , and  $H_2$  with a small amount of  $N_2$  for use as an internal calibration standard. The level of  $H_2$  in the feed ranged from 0 to 50% that corresponded to  $H_2/O_2$  ratios ranging from 0 to 3.0. The amount of  $N_2$  in the feed was always less than 1%. In the range of conditions studied, no flames were observed.

The addition of  $H_2$  (Table 17) during the oxidative dehydrogenation of ethane over a 1.0% Cu – 9.0%  $Cr_2O_3/ZrO_2$  monolith catalyst with less than 1%  $N_2$  dilution at a total feed flow rate of 7 SLPM results in a significant increase in the  $C_2H_4$  selectivity. At a  $C_2H_6/O_2$  ratio of 2.0, the selectivity to  $C_2H_4$  increases from 58% with no  $H_2$  addition to 76% with a  $H_2/O_2$  ratio of 3.0 in the reactor feed. At a  $C_2H_6/O_2$  ratio of 2.4, the selectivity to  $C_2H_4$  increases from 68% with no  $H_2$  addition to 81% with a  $H_2/O_2$  ratio of 3.0 in the reactor feed. The increase in the  $C_2H_4$  selectivity corresponds with a decrease in the selectivity to CO and  $CO_2$ . The selectivity to CO and  $CO_2$  falls proportionally with increasing  $H_2$  in the feed. The selectivity to  $CH_4$  also falls slightly with increasing  $H_2$  addition. The addition of  $H_2$ , however, also results in a decrease in the  $C_2H_6$  conversion which falls from 94% to 81% at a  $C_2H_6/O_2$  ratio of 2.0, and 80% to 66% at a  $C_2H_6/O_2$  ratio of 2.4 as the  $H_2/O_2$  feed ratio increases from 0 to 3. Along with the decrease in the  $C_2H_6$  conversion, the temperature measured at the exit of the catalyst at both  $C_2H_6/O_2$

Table 17: Carbon and hydrogen atom selectivity, conversion,  $C_2H_4$  yield, and temperature for ethane oxidation over a 45 ppi, 1.0% Cu – 9.0%  $Cr_2O_3/ZrO_2$  monolith as a function of the  $H_2/O_2$  ratio at  $C_2H_6/O_2$  ratios of 2.0 and 2.4 at a total flow rate of 7 SLPM with less than 1%  $N_2$  dilution in an autothermal reactor at a pressure of 1.2 atm.

$C_2H_6/O_2$	2.0				2.4			
$H_2/O_2$	0	1	2	3	0	1	2	3
Carbon atom selectivity (%)								
$C_2H_4$	56	64	71	75	68	74	78	81
CO	18	14	11	9	11	9	8	6
$CO_2$	8	6	5	4	8	6	5	4
$CH_4$	9	8	8	7	6	6	5	5
$C_2H_2$	5	3	2	2	1	1	1	1
Other	4	4	3	3	4	4	3	3
Hydrogen atom selectivity (%)								
$H_2$	22	17	11	4	19	9	5	1
$H_2O$	31	33	35	39	31	36	37	42
Conversion (%)								
$C_2H_6$	94	90	86	81	80	78	71	66
$O_2$	100	100	100	100	100	100	100	100
Temperature ( $^{\circ}C$ )								
Front	161	60	55	46	48	28	30	31
Rear	881	860	839	822	849	826	812	795
Carbon atom yield (%)								
$C_2H_4$	53	58	60	61	55	58	55	54

ratios falls with increasing  $H_2$  content in the feed. Thus, the overall production or yield of  $C_2H_4$  in the reaction system is also affected by  $H_2$  addition in the feed since the selectivity to  $C_2H_4$  increases with  $H_2$  addition and the  $C_2H_6$  conversion decreases with the addition of  $H_2$ . At a  $C_2H_6/O_2$  ratio of 2.0, the  $C_2H_4$  yield steadily increases with higher  $H_2/O_2$  ratios in the feed, but the marginal increase decreases at the higher  $H_2/O_2$  ratios. Thus, the selectivity to the desired product,  $C_2H_4$ , increases faster than the decrease in the  $C_2H_6$  conversion with increasing  $H_2$  concentration in the feed. At a  $C_2H_6/O_2$  ratio of 2.4, the yield of  $C_2H_4$  goes through a maximum at a  $H_2/O_2$  of 1.0. This directly results from the fact that at a  $H_2/O_2$  below 1, the  $C_2H_4$  selectivity rises faster than the corresponding decrease in  $C_2H_6$  conversion. However, at a  $H_2/O_2$  ratio of 2 or above, the  $C_2H_4$  selectivity rises slower than the decrease in the conversion of  $C_2H_6$ .

Table 1: Carbon atom and hydrogen atom selectivity, conversion, and temperature for ethane oxidation over various catalysts at several  $C_2H_6/O_2$  ratios with 20%  $N_2$  dilution and a total flow rate of 2 SLPM in an autothermal reactor at a pressure of 1.2 atm.

Catalyst	10 wt. % $Cr_2O_3/\alpha-Al_2O_3$			Pt-10 wt. % $Cr_2O_3/\alpha-Al_2O_3$			9 wt. % $Cr_2O_3/ZrO_2$					6.7 wt. % Cu & 6.7 wt. % Cr/ $ZrO_2$					3 wt. % Pt/ $\alpha-Al_2O_3$				
$C_2H_6/O_2$	1.2	1.5	1.8	1.2	1.5	1.8	1.2	1.5	1.8	2.2	2.4	1.2	1.5	1.8	2.2	2.4	1.2	1.5	1.8	2.2	2.4
Carbon atom selectivity (%)																					
$C_2H_4$	19	44	56	20	45	62	32	55	67	70	70	14	43	62	72	73	31	57	65	64	62
CO	42	30	25	41	30	19	36	18	11	9	9	50	32	17	8	7	40	26	17	16	15
$CO_2$	7	7	6	4	5	8	8	10	12	14	17	4	5	8	11	13	3	3	6	11	14
$CH_4$	14	11	9	14	11	7	13	8	5	3	2	13	10	7	5	4	13	8	6	4	4
$C_2H_2$	16	3	0.3	15	6	1	11	4	1	1	0.3	15	10	5	1	1	10	2	0.4	0.1	0
other	2	5	4	7	4	4	0.3	4	4	3	3	3	0	0	2	3	4	4	7	5	6
Hydrogen atom selectivity (%)																					
$H_2$	56	44	37	58	43	34	47	32	27	25	24	45	32	24	19	18	39	27	22	16	14
$H_2O$	16	17	19	15	17	19	20	24	25	27	30	19	20	21	22	23	24	25	29	36	40
Conversion (%)																					
$C_2H_6$	100	97	81	100	95	82	100	98	90	72	64	100	97	87	72	63	100	95	80	65	57
$O_2$	100	100	99	100	100	100	100	100	100	100	100	100	100	100	98	99	100	100	100	100	99
Temperature (°C)																					
Front	1183	675	228	1249	205	167	1164	1000	830	675	620	1132	1025	1020	380	346	1162	710	512	396	365
Rear	978	898	570	1003	947	992	875	816	775	753	745	892	825	792	768	757	1013	923	885	866	853

## EXAMPLES

**Example 1:** The oxidative dehydrogenation of ethane was examined over a variety of catalysts supported on ceramic foam monoliths at a flowrate of 2 standard liters per minute (SLPM) which corresponds to a contact time of approximately 15 ms (GHSV = 200,000  $hr^{-1}$ ). The ceramic foam monolith supports (alpha-alumina or magnesia stabilized zirconia) were obtained from Vesuvius Hi-Tech Ceramics and contain 45 ppi (pores per linear inch). Chromium was deposited on the support surface by exposing the ceramic to a liquid solution containing chromium ions such as aqueous chromium nitrate. Platinum was deposited on the support surface by exposing the ceramic to a liquid solution containing platinum ions such as aqueous chloroplatinic acid. Copper was deposited on the support surface by exposing the ceramic to a liquid solution containing copper ions such as aqueous copper nitrate. Between depositions, the catalysts were calcined in air.

Table 1 shows product carbon and hydrogen atom selectivity, conversion, and reaction temperature at several  $C_2H_6/O_2$  ratios in the feed gas with 20%  $N_2$  dilution for 10 wt. %  $Cr_2O_3/\alpha-Al_2O_3$ , 9 wt. %  $Cr_2O_3/ZrO_2$ , 3 wt. %  $Pt/\alpha-Al_2O_3$ , 6.7 wt. %  $Cu$  - 6.7 wt. %  $Cr/ZrO_2$ , and  $Pt$  (0.05 wt. %) modified 10 wt. %  $Cr_2O_3/\alpha-Al_2O_3$  catalysts. At a  $C_2H_6/O_2$  ratio of 1.2, the 9 wt. %  $Cr_2O_3/Al_2O_3$  and  $Pt$  modified 10 wt. %  $Cr_2O_3/Al_2O_3$  catalysts have a  $C_2H_4$  selectivity around 20% compared to the 30% and 32% selectivity to  $C_2H_4$  seen for the 3 wt. %  $Pt/\alpha-Al_2O_3$  and 9 wt. %  $Cr_2O_3/ZrO_2$  catalysts respectively. The  $CO$  selectivity is approximately 40% for all the catalysts except for the  $Cr_2O_3/ZrO_2$  catalyst which showed a slightly lower selectivity to  $CO$  of approximately 35% and the  $Cu$  modified catalyst which showed a slightly higher selectivity to  $CO$  of ~50%. For the selectivity to  $CO_2$ , a significant difference can be seen between the  $Cr_2O_3$  and  $Pt$  catalysts with more  $CO_2$  formed over the  $Cr_2O_3$  than over  $Pt$ . The  $CO_2$  selectivity for the  $Pt$ -modified chromium oxide catalyst falls directly between the two single component catalysts. The  $CH_4$  selectivity, however, is essentially the same for all the catalysts at approximately 13%. The selectivity to  $C_2H_2$  is slightly higher for the  $Cr_2O_3/Al_2O_3$  and the  $Cu$  modified catalyst than the three other catalysts. At a  $C_2H_6/O_2$  ratio of 1.2, the highest selectivity to  $H_2$  is about 56% for the  $Cr_2O_3/Al_2O_3$  and  $Pt$ -modified  $Cr_2O_3/Al_2O_3$  catalysts. The  $H_2$  selectivity for the  $Cr_2O_3/ZrO_2$  was 47% and the  $Pt/Al_2O_3$  catalyst was 39%. The corresponding selectivity to  $H_2O$  is higher for the  $Pt/Al_2O_3$  and  $Cr_2O_3/ZrO_2$  catalysts than the two  $Cr_2O_3/Al_2O_3$  catalysts.

Similar trends between the catalysts exist at higher  $C_2H_6/O_2$  ratios. The  $Cr_2O_3/ZrO_2$  catalyst and the  $Cu$  modified  $Cr_2O_3/ZrO_2$  catalyst show the best  $C_2H_4$  selectivity at the highest  $C_2H_6/O_2$  ratios with the  $Cu$  modified  $Cr_2O_3/ZrO_2$  catalyst showing the lowest selectivity to  $CO$ . The  $C_2H_6$  conversion and  $C_2H_4$  yield is higher over the  $Cr_2O_3/ZrO_2$  catalyst and the  $Cu$  modified  $Cr_2O_3/ZrO_2$  catalyst than over the  $Pt$

catalyst; the difference increases with increasing ratios of  $C_2H_6/O_2$  in the feed. At  $C_2H_6/O_2$  ratios of 1.2 and 1.5, the  $C_2H_4$  selectivity for the  $Cr_2O_3/ZrO_2$  and the  $Pt/Al_2O_3$  catalysts is essentially the same with a lower  $C_2H_4$  selectivity for the Cu modified  $Cr_2O_3/ZrO_2$  catalyst. But at the higher  $C_2H_6/O_2$  ratios, the selectivity to  $C_2H_4$  is higher over the chromium oxide and Cu modified chromium oxide catalysts at >70% compared to <65% over the Pt catalyst. The  $H_2$  selectivity for the  $Cr_2O_3/ZrO_2$  catalyst and the Cu modified  $Cr_2O_3/ZrO_2$  catalyst is also higher at all  $C_2H_6/O_2$  ratios, especially at the higher  $C_2H_6/O_2$  ratios. The CO selectivity is lower for the chromium oxide-zirconia catalyst and at the higher  $C_2H_6/O_2$  ratios is approximately half of the CO selectivity for the Pt catalyst. This reduction in CO production is even more evident at the higher  $C_2H_6/O_2$  ratios over the Cu modified  $Cr_2O_3/ZrO_2$  catalyst. However, the selectivity towards complete combustion products,  $CO_2$  and  $H_2O$ , is higher over the  $Cr_2O_3/ZrO_2$ .

All catalysts exhibit similar  $C_2H_6$  conversions with lower conversions at the higher  $C_2H_6/O_2$  ratios. At  $C_2H_6/O_2$  ratios greater than 1.2, the chromium oxide containing catalysts all show a slightly higher  $C_2H_6$  conversion than the Pt monolith. In all cases,  $O_2$  is essentially completely consumed.

**Example 2:** The oxidative dehydrogenation of ethane was examined over a large variety of catalysts supported on ceramic foam monoliths at flow rates ranging from 2 to 4 standard liters per minute (SLPM) which corresponds roughly to catalyst contact times of 5-15 ms (GHSV = 80,000 – 200,000  $hr^{-1}$ ).

Table 2 shows product carbon and hydrogen atom selectivity, conversion, and reaction temperature at a  $C_2H_6/O_2$  ratio of 2.0 in the feed gas with 20%  $N_2$  dilution at a total feed flow rate of 2.0 SLPM for the oxidative dehydrogenation of ethane over single component catalysts. The  $Cr_2O_3$ , CuO, and  $MnO_x$  catalysts on a  $ZrO_2$  monolith have



Table 2: Carbon atom and hydrogen atom selectivity, conversion, and temperature for ethane oxidation over various single component catalysts at a  $C_2H_6/O_2$  ratio of 2.0 with 20%  $N_2$  dilution and a total flow rate of 2 SLPM in an autothermal reactor at a pressure of 1.2 atm.

Catalyst	3 wt. % $Pt/Al_2O_3$	9 wt. % $Cr_2O_3/ZrO_2$	11.2 wt. % $CuO/ZrO_2$	9.7 wt. % $Ni/ZrO_2$	9.1 wt. % $FeO_x/ZrO_2$	8.1 wt. % $MnO_x/ZrO_2$
Carbon Atom Selectivity (%)						
$C_2H_4$	63	68	68	2	51	68
CO	22	10	10	89	31	7
$CO_2$	6	13	10	8	10	11
$CH_4$	5	4	7	0.5	6	7
$C_2H_2$	1	1	2	0	0	3
Other	3	3	3	0	2	4
Hydrogen Atom Selectivity (%)						
$H_2$	22	26	17	91	43	19
$H_2O$	25	26	22	6	13	22
Conversion (%)						
$C_2H_6$	71	81	82	45	74	83
$O_2$	100	100	100	100	100	100
Temperature (C)						
Front	939	745	392	73	268	985
Rear	836	763	807	749	745	822

essentially the same reaction results under these conditions with a  $C_2H_4$  selectivity of ~68% with over 81% conversion of the ethane feed. These catalysts,  $Cr_2O_3$ ,  $CuO$ , and  $MnO_x$ , also have very low selectivity to CO of 10%, 10%, and 7%, respectively; along with a corresponding higher  $CO_2$  selectivity than the other single component catalysts. The 3 wt. %  $Pt/\alpha-Al_2O_3$  catalyst had a slightly lower selectivity to  $C_2H_4$  and lower conversion of  $C_2H_6$  than the  $Cr_2O_3$ ,  $CuO$ , and  $MnO_x$  catalysts. Additionally, the  $Pt/Al_2O_3$  catalyst also had a higher selectivity to CO and lower selectivity to  $CO_2$  than the three transition metal oxide catalysts. The 9.1 wt. %  $FeO_x/ZrO_2$  catalyst also had a lower selectivity to  $C_2H_4$  (51%) and lower  $C_2H_6$  conversion (74%) along with a significantly higher selectivity to CO (31%) than the  $Cr_2O_3$ ,  $CuO$ , and  $MnO_x$  catalysts. In contrast to all the other single component catalysts, the 9.7 wt. % Ni on a  $ZrO_2$  monolith produced primarily syngas products, CO and  $H_2$ , and not oxidative dehydrogenation products,  $C_2H_4$  and  $H_2O$ .

**Example 3:** Table 3 shows the results for the oxidative dehydrogenation of ethane over  $\text{Cr}_2\text{O}_3/\text{ZrO}_2$  monolith catalyst with the addition of a single promoter including Ag, Cu,  $\text{FeO}_x$ , Ni,  $\text{MnO}_x$  and MgO. The reaction results for a  $\text{C}_2\text{H}_6/\text{O}_2$  ratio of 2.0 with 20%  $\text{N}_2$  dilution at a total flow rate of 2 SLPM show that the addition of the promoters to the  $\text{Cr}_2\text{O}_3/\text{ZrO}_2$  catalyst can change the product selectivities and conversion over the catalyst. The addition of Cu or Ag to the  $\text{Cr}_2\text{O}_3/\text{ZrO}_2$  catalyst does not significantly affect the product selectivities or reactant conversions. The addition of  $\text{FeO}_x$  or MgO to the  $\text{Cr}_2\text{O}_3/\text{ZrO}_2$  catalyst results in a slight decrease in the ethane conversion from 81% to 75% and 78%, respectively, but does not significantly affect the product selectivities. In contrast, the addition of  $\text{MnO}_x$  to the  $\text{Cr}_2\text{O}_3/\text{ZrO}_2$  catalyst results in a decrease in the  $\text{C}_2\text{H}_4$  selectivity to 61% from 68% and a corresponding increase in the CO selectivity to 22% from 13%. The ethane conversion of the 0.8 wt. %  $\text{MnO}_x$  - 8.0 wt. %  $\text{Cr}_2\text{O}_3/\text{ZrO}_2$  catalyst, however, is the same as the 9.0 wt. %  $\text{Cr}_2\text{O}_3/\text{ZrO}_2$ .

Table 3: Carbon atom and hydrogen atom selectivity, conversion, and temperature for ethane oxidation over various catalysts at a  $\text{C}_2\text{H}_6/\text{O}_2$  ratio of 2.0 with 20%  $\text{N}_2$  dilution and a total flow rate of 2 SLPM in an autothermal reactor at a pressure of 1.2 atm.

Catalyst	1.3 wt. % Cu - 13.0 wt. % $\text{Cr}_2\text{O}_3/\text{ZrO}_2$	2.2 wt. % Ag - 11.0 wt. % $\text{Cr}_2\text{O}_3/\text{ZrO}_2$	0.7 wt. % $\text{FeO}_x$ - 7.0 wt. % $\text{Cr}_2\text{O}_3/\text{ZrO}_2$	0.7 wt. % Ni - 7.0 wt. % $\text{Cr}_2\text{O}_3/\text{ZrO}_2$	0.8 wt. % $\text{MnO}_x$ - 8.0 wt. % $\text{Cr}_2\text{O}_3/\text{ZrO}_2$	0.7 wt. % MgO - 7.0 wt. % $\text{Cr}_2\text{O}_3/\text{ZrO}_2$
Carbon Atom Selectivity (%)						
$\text{C}_2\text{H}_4$	68.	68	69	46	61	68
CO	13	12	11	41	22	13
$\text{CO}_2$	9	10	10	9	6	10
$\text{CH}_4$	6	6	5	3	6	5
$\text{C}_2\text{H}_2$	2	2	0	0	1	1
other	3	3	4	1	3	3
Hydrogen Atom Selectivity (%)						
$\text{H}_2$	20	22	20	45	25	20
$\text{H}_2\text{O}$	22	22	24	20	23	23
Conversion (%)						
$\text{C}_2\text{H}_6$	80	80	75	60	81	78
$\text{O}_2$	100	100	100	100	100	100
Temperature (°C)						
Front	545	939	1044	988	999	934
Rear	856	836	833	798	821	796

**Example 4:** Table 4 shows the results for multi-component catalysts for the oxidative dehydrogenation of ethane for a  $C_2H_6/O_2$  ratio of 2.0 with 20%  $N_2$  dilution at a total flow rate of 2 SLPM. The addition of  $MgO$ ,  $FeO_x$ , and  $MnO_x$  to a  $Cu/Cr_2O_3/ZrO_2$  results in a lower selectivity to  $C_2H_4$  and corresponding higher selectivity to  $CO$  along with a lower  $C_2H_6$  conversion than the 1.3 wt. %  $Cu$  – 13.0 wt. %  $Cr_2O_3$  on a  $ZrO_2$  monolith. The addition of  $Ni$  to the  $Cu/Cr_2O_3/ZrO_2$  catalyst also resulted in a slightly lower  $C_2H_4$  selectivity, but the addition of  $Ni$  did not significantly affect the  $C_2H_6$  conversion.

The addition of the  $Cu$  to the  $Cr_2O_3/ZrO_2$  catalyst does not significantly affect the product selectivity or reactant conversions as noted above. The addition of  $Cu$ , however, did significantly increase the activity of the  $CuO/Cr_2O_3/ZrO_2$  catalyst especially at higher flow rates,  $N_2$  dilutions, and  $C_2H_6/O_2$  ratios. The 1.3 wt. %  $Cu$  – 13.0 wt. %

Table 4: Carbon atom and hydrogen atom selectivity, conversion, and temperature for ethane oxidation over various catalysts at a  $C_2H_6/O_2$  ratio of 2.0 with 20%  $N_2$  dilution and a total flow rate of 2 SLPM in an autothermal reactor at a pressure of 1.2 atm.

Catalyst	1.1 wt. % $Cu$ – 11.0 wt. % $MnO_x/ZrO_2$	5.3 wt. % $MgO$ – 0.9 wt. % $Cu$ – 8.9 wt. % $Cr_2O_3/ZrO_2$	1.9 wt. % $Ni$ – 0.9 wt. % $Cu$ – 9.3 wt. % $Cr_2O_3/ZrO_2$	2.1 wt. % $FeO_x$ – 1.0 wt. % $Cu$ – 10.3 wt. % $Cr_2O_3/ZrO_2$	1.7 wt. % $MnO_x$ – 0.8 wt. % $Cu$ – 8.6 wt. % $Cr_2O_3/ZrO_2$
<b>Carbon Atom Selectivity (%)</b>					
$C_2H_4$	67	63	65	65	63
$CO$	8	22	13	19	22
$CO_2$	11	6	9	7	7
$CH_4$	6	5	6	5	5
$C_2H_2$	3	1	1	1	1
other	4	3	6	3	3
<b>Hydrogen Atom Selectivity (%)</b>					
$H_2$	19	23	23	24	23
$H_2O$	22	24	21	23	24
<b>Conversion (%)</b>					
$C_2H_6$	72	72	81	76	72
$O_2$	100	100	100	100	100
<b>Temperature (C)</b>					
Front	849	934	988	999	934
Rear	856	796	798	821	796

$\text{Cr}_2\text{O}_3/\text{ZrO}_2$  catalyst was able to achieve stable operation at a  $\text{C}_2\text{H}_6/\text{O}_2$  ratio of 2.4 with 50%  $\text{N}_2$  dilution at a total flow rate of 10 SLPM with no signs of deactivation. In contrast, the 9 wt. %  $\text{Cr}_2\text{O}_3/\text{ZrO}_2$  catalyst was only able to achieve stable, non-deactivating behavior at a  $\text{C}_2\text{H}_6/\text{O}_2$  ratio of 2.4 with 50%  $\text{N}_2$  dilution at a total flow rate of less than 4 SLPM. It was also found that the addition of the Cu promoter to a  $\text{MnO}_x/\text{ZrO}_2$  catalyst did not result in the same dramatic increase in catalyst activity.

**Example 5:** Under some conditions, reaction is not sustained indefinitely over some of the supported chromium oxide catalysts. The onset of extinction depends on the composition of the catalyst, the  $\text{C}_2\text{H}_6/\text{O}_2$  ratio, the support material, the weight loading of the catalyst, the flowrate, the  $\text{N}_2$  dilution, and the preheat of the feed.

The time to extinction is shown in Table 5 as a function of  $\text{C}_2\text{H}_6/\text{O}_2$  ratio with 20% reactant dilution at a flowrate of 2 SLPM for the various catalysts. The sustained activity of the  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  and the  $\text{Pt}/\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3/\text{ZrO}_2$  catalysts differ in that the  $\text{Pt}/\text{Al}_2\text{O}_3$ , Cu modified  $\text{Cr}_2\text{O}_3/\text{ZrO}_2$ , and the 9 wt. %  $\text{Cr}_2\text{O}_3/\text{ZrO}_2$  catalyst sustain reaction for a much longer period of time than the other catalyst compositions examined. Like the Pt monolith, the 10 wt. %  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  catalyst at a  $\text{C}_2\text{H}_6/\text{O}_2$  ratio of 1.2 with 20%  $\text{N}_2$  at a flowrate of 2 SLPM has shown sustained reaction for very long periods of time with no deactivation and product selectivity changes. However, at a  $\text{C}_2\text{H}_6/\text{O}_2$  ratio of 1.5, the reaction is sustained for only 1.6 hours. Before extinction of the reaction, the product selectivity and reactant conversions are constant over the entire time period. The catalyst temperature falls slightly in the first 1.25 hours and then rapidly decreases until the reaction extinguishes. At a  $\text{C}_2\text{H}_6/\text{O}_2$  ratio of 1.8 with 20%  $\text{N}_2$  dilution at 2 SLPM, the reaction over the  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  monolith extinguishes after only 5-10 minutes.

Table 5: The reactive lifetime of the various catalysts as a function of  $C_2H_6/O_2$  ratio in the feed with 20%  $N_2$  dilution with a total feed flow rate of 2 SLPM in an autothermal reactor at a pressure of 1.2 atm.

Fuel/ $O_2$	1.2	1.5	1.8	2.0	2.2	2.4
Catalyst	Lifetime (hrs)					
3 % Pt/ $\alpha$ - $Al_2O_3$	> 5.0*	> 5.0*	> 5.0*	> 5.0*	> 5.0*	> 5.0*
9% $Cr_2O_3/ZrO_2$	> 2.0*	> 2.0*	> 6.0*	> 2.0*	> 2.0*	> 2.0*
2% $Cr_2O_3/ZrO_2$	> 2.0*	> 2.0*	0.1	---	---	---
10% $Cr_2O_3/\alpha$ - $Al_2O_3$	> 4.0*	1.6	0.1	---	---	---
1.5% $Cr_2O_3/\alpha$ - $Al_2O_3$	0.1	< 0.1	---	---	---	---
6.7% Cu - 6.7% $Cr_2O_3/ZrO_2$	> 2.0*	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 2.0*
10% $Cr_2O_3/\alpha$ - $Al_2O_3$ Pellets	> 1.0*	> 7.5*	0.2	0.2	---	---
1.3 % Cu - 13.0% $Cr_2O_3/ZrO_2$	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 5.0*
9.1 % FeO/ $ZrO_2$	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 1.0*
8.1 % MnO/ $ZrO_2$	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 1.0*
9.7 % Ni/ $ZrO_2$	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 1.0*
11.2 % CuO/ $ZrO_2$	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 1.0*	> 1.0*
Pt-10% $Cr_2O_3/\alpha$ - $Al_2O_3$	> 1.0*	> 7.0*	9.0	---	---	---

\* Catalyst did not show any signs of deactivation

In contrast to the  $Cr_2O_3/Al_2O_3$  catalyst, the reaction was sustained under these conditions for the 9 wt. %  $Cr_2O_3/ZrO_2$  catalyst and the Cu modified  $Cr_2O_3/ZrO_2$  catalyst for longer periods, similar to the Pt/ $Al_2O_3$  monolith catalyst. Like the Pt catalyst, a 9 wt. %  $Cr_2O_3/ZrO_2$  catalyst showed non-deactivating steady state behavior up to a  $C_2H_6/O_2$  ratio of 2.4 with 20%  $N_2$  dilution at a total flowrate of 2 SLPM which is well outside of the flammability range for this system. At a  $C_2H_6/O_2$  ratio of 1.8 with 20%  $N_2$  dilution at 2 SLPM, the 9 wt. %  $Cr_2O_3/ZrO_2$  monolith catalyst did not show any deactivation after 5 hours of continuous operation, while the reaction quickly extinguished under these condition for lower chromium oxide loadings on  $ZrO_2$  and on all  $Cr_2O_3/Al_2O_3$  catalysts. At a  $C_2H_6/O_2$  ratio of 1.5 with 50%  $N_2$  dilution at 2 SLPM, the Cu modified  $Cr_2O_3/ZrO_2$  monolith catalyst did not show any deactivation for over 7 hours of continuous operation. The chromium oxide loading of the monoliths can significantly affect the catalysts. For chromium oxide supported on  $ZrO_2$  and  $Al_2O_3$ , the activity of the catalyst increases with the chromium oxide loading.

The other transition metal oxide catalysts (11.2 wt. % Cu/ $ZrO_2$ , 9.7 wt. %

Ni/ZrO<sub>2</sub>, 9.1 wt. % FeO<sub>x</sub>/ZrO<sub>2</sub>, and 8.1 wt. % MnO<sub>x</sub>/ZrO<sub>2</sub>) are able to sustain reaction for more than one hour under these conditions. Additionally, the addition of the promoters (Ag, Ni, Mn, Mg, Fe, Cu, their oxides, and combinations thereof) to the Cr<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> led to stable operation for several hours with no signs of deactivation at a C<sub>2</sub>H<sub>6</sub>/O<sub>2</sub> ratio of 2.4 with 20% N<sub>2</sub> dilution at a total flow rate of 2 SLPM.

The addition of very small amounts of Pt (> 0.001g, ~0.05 wt. %), as a co-catalyst, was examined for its influence on the ability of the supported chromium oxide catalysts to sustain reaction for extended periods. Table 5 shows the time to extinction for Pt-modified Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and unmodified Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> monolith catalysts at several C<sub>2</sub>H<sub>6</sub>/O<sub>2</sub> ratios with 20% N<sub>2</sub> dilution at a flowrate of 2 SLPM. The activity of Pt-coated monoliths for the oxidative dehydrogenation is relatively independent of the Pt loading, even for very small amounts of Pt [Haubein, N., *Effects of Support Material and Pt Loading on the Catalytic Oxidative Dehydrogenation of Ethane*; University of Delaware, 1997]. The addition of Pt significantly increases the length of time that reaction can be sustained over the Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. However, the Pt-modified Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst still extinguished rapidly at the higher C<sub>2</sub>H<sub>6</sub>/O<sub>2</sub> ratios unlike the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.

The surface area can also influence the temporal behavior of the catalyst. The surface area of the monolith supports is approximately 200 cm<sup>2</sup> per gram, which is approximately 400 cm<sup>2</sup> of total surface area for the monoliths used here. The total surface area can be increased by replacing the monolith with a packed bed of 3 mm Al<sub>2</sub>O<sub>3</sub> pellets. The surface area of blank  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> pellets is 9 m<sup>2</sup> per gram which results in a catalyst bed with approximately 27 m<sup>2</sup> of total surface area. The packed bed contained 60 Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> pellets, which was approximately equal in total weight to the chromium oxide monolith catalyst and resulted in an approximate bed depth of 1.5 cm.

Table 6: The reactive lifetime of the various catalysts as a function of the total feed flow rate at several  $C_2H_6/O_2$  ratios in the feed with 20%  $N_2$  dilution in an autothermal reactor at a pressure of 1.2 atm.

Fuel/ $O_2$ Flowrate (SLPM)	1.2 1.0	1.2 2.0	1.2 3.0	1.5 1.0	1.5 2.0	1.5 3.0	1.8 1.0	1.8 2.0	1.8 3.0
Catalyst	Lifetime (hrs)								
3 % Pt/ $\alpha-Al_2O_3$	> 2.0*	> 5.0*	> 2.0*	> 2.0*	> 5.0*	> 2.0*	> 2.0*	> 5.0*	> 2.0*
10% $Cr_2O_3/\alpha-Al_2O_3$	> 1.0*	> 4.0*	< 0.2	7.0	1.6	< 0.1	?	0.1	—
1.5% $Cr_2O_3/\alpha-Al_2O_3$	> 6.5	0.1	—	0.1	< 0.1	—	—	—	—
6.7% Cu -	?	*	*	?	*	*	?	*	*
6.7% $Cr_2O_3/ZrO_2$									
9% $Cr_2O_3/ZrO_2$	> 2.0*	> 2.0*	> 6.0*	> 3.0*	> 2.0*	> 3.0*	> 1.0*	> 6.0*	2.8
4% $Cr_2O_3/ZrO_2$	> 2.0*	> 2.0*	> 5.0*	> 2.0*	> 9.0*	1.5	?	?	?
2% $Cr_2O_3/ZrO_2$	*	> 2.0*	?	?	?	?	?	0.1	—

\* Catalyst did not show any signs of deactivation

Reaction was sustained over the 10 wt. %  $Cr_2O_3/\alpha-Al_2O_3$  pellets for more than about 7.5 hours with no sign of deactivation or changes in the product selectivity at a  $C_2H_6/O_2$  ratio of 1.5 with 20%  $N_2$  dilution at a flowrate of 2 SLPM. Under the same conditions, the 10 wt. %  $Cr_2O_3/Al_2O_3$  monolith extinguished in 1.6 hours. In addition to the difference in reactive lifetimes, the chromium oxide pellet catalyst displayed a slightly higher selectivity to  $C_2H_4$  and lower selectivity to CO. The chromium oxide pellets also displayed a slightly lower  $C_2H_6$  conversion, 94%, compared to 96%  $C_2H_6$  conversion over the chromium oxide monolith. Therefore, in addition to the composition of the ceramic support, the total surface area of the catalyst can also have a significant impact upon the behavior of the supported chromium oxide catalyst.

The feed flowrate strongly affects the sustainability of reaction over the chromium oxide catalysts as shown in Table 6. For the 10 wt. %  $Cr_2O_3/Al_2O_3$  catalyst at a  $C_2H_6/O_2$  ratio of 1.5 with 20%  $N_2$  dilution, the reaction was sustained for 7 hours at 1 SLPM, 1.6 hours at 2 SLPM, and only a couple of minutes at a flowrate of 3 SLPM. When the chromium oxide loading is reduced, the activity of the catalyst decreases accordingly. For a 1.5 wt. %  $Cr_2O_3/\alpha-Al_2O_3$  monolith, reaction at 2 SLPM with 20%  $N_2$  dilution could not be sustained even at a  $C_2H_6/O_2$  ratio of 1.2. The total flowrate had to

be reduced by 50% to 1 SLPM before reaction over the low chromium oxide containing catalyst was sustained for an extended period of time (>6 hrs.) In spite of the lower flowrate and hence longer contact time, the catalyst did not achieve steady state. Throughout the time survey, the catalyst showed signs of deactivation with the conversion of  $C_2H_6$  and  $O_2$  falling with time on stream.

For the  $Cr_2O_3/ZrO_2$  catalysts, the flowrate also strongly affects the catalyst's lifetime. At a  $C_2H_6/O_2$  ratio of 1.5 with 20%  $N_2$  dilution over the 4 wt. %  $Cr_2O_3/ZrO_2$  monolith catalyst, the reaction was only sustained for 1.5 hours at a flowrate of 3 SLPM, compared to over 9 hours at 2 SLPM. Similar decreases in the lifetime with increasing flowrate, and correspondingly shorter contact time, can be seen for the 9 wt. %  $Cr_2O_3/ZrO_2$  catalyst at the higher  $C_2H_6/O_2$  ratios. The Cu modified  $Cr_2O_3/ZrO_2$  catalyst showed no signs of deactivation for  $C_2H_6/O_2$  ratios up to 2.4 and total flow rates up to 4 SLPM.

In addition to the lifetime of the catalyst, the flowrate affects the product selectivity and ethane conversion shown in Tables 7 and 8. As the flowrate increases, the selectivity to  $C_2H_4$  decreases and the selectivity to  $C_2H_2$  increases; the  $H_2O$  selectivity decreases; and the conversion increases slightly. The most significant effect of increasing the flowrate can be observed by examining the temperatures measured at the front and back of the catalyst. At the lowest flow rates, the temperature on the front face of the catalyst exceeds the temperature at the rear face of the catalyst; while at the higher flow rates, the front temperature is much less than the rear temperature.

The lifetime of the chromium oxide catalysts is also influenced by the  $N_2$  dilution in the feed mixture. At 50%  $N_2$  dilution at 2 SLPM with a  $C_2H_6/O_2$  ratio of 1.2, the reaction over the 10 wt. %  $Cr_2O_3/\alpha-Al_2O_3$  catalyst was only sustained for 20 minutes before the reaction rapidly extinguished, and at a  $C_2H_6/O_2$  ratio of 1.5, the reaction



## We claim:

1. A process to produce olefins which comprises reacting hydrocarbons and an oxygen containing gas in the presence of a catalyst comprising a chromium containing compound, a copper containing compound, a manganese containing compound, or combinations thereof supported on a monolith.
2. A process as claimed in claim 1 wherein said reacting hydrocarbons comprise at least one saturated hydrocarbon containing 2 to 6 carbon atoms.
3. A process as claimed in claim 1 wherein oxygen gas comprises 5 to 40% (by volume) of the reacting feed.
4. A process as claimed in claim 1, wherein the catalyst contact time is less than 0.02 seconds.
5. The process as claimed in claim 1, wherein said chromium containing compound is a chromium oxide stable at temperature in excess of about 900° C.
6. The process as claimed in claim 1, wherein said monolith is ceramic and has a honeycomb or foam structure.
7. The process as claimed in claim 1, wherein said monolith is composed of  $Al_2O_3$ ,  $SiO_2$ , Mg-stabilized  $ZrO_2$ , Y-stabilized  $ZrO_2$ , or mixtures thereof.
8. The process as claimed in claim 1, wherein said monolith is composed of Mg-stabilized  $ZrO_2$ .
9. The process as claimed in claim 6, wherein said monolith has a foam structure and has about 20 to about 100 pores per linear inch.
10. The process as claimed in claim 6, wherein said catalyst contains substantially no platinum.
11. The process as claimed in claim 1, wherein said monolith further comprises

at least one promoter selected from the group consisting of Mn, Mg, Ni, Fe, Ag, Pt, and oxides thereof.

12. The process as claimed in claim 1, wherein said catalyst is present in the substantial absence of platinum.

13. The process as claimed in claim 1, wherein the ratio of atoms of Cu to Cr is between about 1:100 and about 1:2.

14. The process as claimed in claim 1, wherein the ratio of atoms of Cu to Cr is between 1:15 and 1:5.

15. The process as claimed in claim 4 wherein the reacting hydrocarbons and oxygen containing gas contains at least one hydrocarbon at ambient temperature.

16. The process as claimed in claim 4 wherein the reacting hydrocarbons and oxygen containing gas contains at least one hydrocarbon at a temperature below about 400°C.

17. The process as claimed in claim 1 wherein the oxygen containing gas comprises at least one of N<sub>2</sub>, Ar, He, CO<sub>2</sub>, and H<sub>2</sub>O.

18. The process as claimed in claim 1 wherein the oxygen containing gas also contains H<sub>2</sub>.

19. A catalyst which comprises a monolith impregnated with a Cr containing compound.

20. The catalyst as claimed in claim 19, wherein said monolith is ceramic and has a honeycomb or foam structure.

21. The catalyst as claimed in claim 19, wherein the monolith is a ceramic foam and contains about 20 to about 100 pores per linear inch.

22. The catalyst as claimed in claim 19, wherein said Cr containing compound is

Cr oxide.

23. The catalyst as claimed in claim 22, wherein said monolith is composed of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , Mg-stabilized  $\text{ZrO}_2$  or Y-stabilized  $\text{ZrO}_2$ .

24. The catalyst as claimed in claim 19, wherein said monolith is composed of Mg-stabilized  $\text{ZrO}_2$ .

25. The catalyst as claimed in claim 19, wherein copper or copper oxide is present.

26. The catalyst as claimed in claim 25, wherein the ratio of atoms of Cu to Cr is between about 1:100 and about 1:2.

27. The catalyst as claimed in claim 25, wherein the ratio of atoms of Cu to Cr is between 1:15 and 1:5.

## INTERNATIONAL SEARCH REPORT

 International application No.  
PCT/US00/01771

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : Please See Extra Sheet.

US CL : 585/654, 658; 502/305, 308, 317, 318, 319, 320, 324, 345, 346

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 585/654, 658; 502/305, 308, 317, 318, 319, 320, 324, 345, 346

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST

search terms: oxidative dehydrogenation, copper, manganese, chromium, foam

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X — Y	US 4,751,336 A (JEZL et al) 14 June 1988 (14/06/88), see column 5, lines 35-65, column 7, lines 36-44, column 8, lines 4-20 and 21-30, column 28, lines 35-37 and column 4, lines 45-48.	1-5, 7, 11-19, 22, 23, 25-27 6, 8-10, 20, 21, 24
Y,P	US 5,905,180 A (YOKOYAMA et al) 18 May 1999 (18/05/99), see abstract, lines 1-3, column 1, lines 64-67 and column 3, lines 1-60.	6, 9, 10, 21
X — Y	US 4,810,685 A (TWIGG et al) 07 March 1989 (07/03/89), see column 2, lines 62-68, column 4, lines 40-45, column 5, lines 60-61 and column 8, lines 3-14.	19, 20, 22, 23, 25-27 21, 24



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	* T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A document defining the general state of the art which is not considered to be of particular relevance	* X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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* O document referring to an oral disclosure, use, exhibition or other means	
* P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

25 MARCH 2000

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18 APR 2000

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/01771

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,162,234 A (GRASSELLI et al) 24 July 1979 (24/07/79), See entire document.	1-27
A	US 4,711,870 A (YAMADA et al) 08 December 1987, see column 4, lines 22-24 and 41-53 and column 5, lines 8-10.	19-27
A	US 5,439,859 A (DURANTE et al) 08 August 1995 (08/08/95), see entire document.	1-27
A	US 5,306,411 A (MAZANEC et al) 26 April 1994 (26/04/94), see entire document.	1-27
A	US 5,591,315 A (MAZANCE et al) 07 January 1997 (07/01/97), see entire document.	1-27
Y	US 5,137,862 A (MACKRODT et al) 11 August 1992 (11/08/92), see column 3, lines 67-68 and column 4, lines 1-8.	8, 24

**INTERNATIONAL SEARCH REPORT**

International application No.  
PCT/US00/01771

**A. CLASSIFICATION OF SUBJECT MATTER:**  
**IPC (7):**

**C07C 5/327, 5/333; B01J 23/16, 23/24, 23/26, 23/32, 23/34, 23/72**